

Minium from Broken Hill, New South Wales.

By BRIAN J. SKINNER, B.Sc., M.A., Ph.D., and E. MAUD MCBRIAR.
Geology Department, University of Adelaide, South Australia.

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Summary. Minium occurs at Broken Hill, New South Wales, as pseudomorphs after cerussite, formed during fires in the mine. It is tetragonal with $a = 8.824 \text{ \AA}$. and $c = 6.564 \text{ \AA}$.; sp. gr. 8.2 ± 0.2 . The Broken Hill minium appears identical in physical properties with synthetic Pb_3O_4 described by other workers.

MINIUM (Pb_3O_4) occurs extensively in the upper workings of the central portion of the Broken Hill mining field, as brilliant scarlet pseudomorphs after cerussite or partially replacing the cerussite. Early descriptions of the mineralogy of Broken Hill do not mention the occurrence of minium. However, after large underground fires in the early part of this century, minium was found extensively in the fire zones. It appears to have formed only from lead carbonate, as there is no evidence that either the sulphate or sulphide were converted to Pb_3O_4 . It seems certain that the minium at Broken Hill was formed by the oxidation of cerussite through the agency of mine fires. If any minium formed by other agencies is present, it must be exceedingly rare, because it has not, to our knowledge, been recorded in previous mineralogical studies.

Minium forms perfect pseudomorphs after cerussite, even to the extent of preserving the cerussite cleavages, and in this case has the appearance of a true single crystal. However, rotation X-ray photographs of the pseudomorphs about the axes of the original cerussite crystal give normal powder patterns. This indicates that the minium grains replacing the cerussite are randomly oriented, and further, since the diffraction lines are of even intensity throughout, that the grain size of the minium is extremely small.

Partial replacement of the cerussite by minium is common (fig. 1). We could not detect any tendency towards preferential replacement along specific crystal directions. Rather, the variations in the extent of replacement appear to be related to the channel-ways in the rock through which gases could enter or escape. Thus, crystals growing in a vugh are more extensively replaced on those portions projecting freely into the

vugh, while at the base of the crystals, where they are extensively intergrown, replacement is much less.

Chemical analysis of a specimen from the old Central Mine (Geol. Dept. Univ. of Adelaide No. 1193) gave 89.94 % Pb, 0.2 % Fe, < 0.1 %

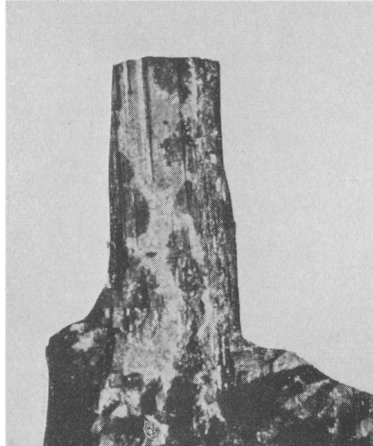


FIG. 1. Minium (appears dark grey) pseudomorphically replacing cerussite (light grey). The crystal is 3 mm. in length.

Zn; CO₂ absent. This is very close to the theoretical 90.67 % Pb for Pb₃O₄; although O was not specifically determined, it appears that the specimen analysed is very close to stoichiometric proportions.

The specific gravity was determined on the Berman Torsion Balance, using toluene as the immersion liquid. Ten measurements gave a value of 8.2 ± 0.2 .

Excellent X-ray powder diffraction photographs were obtained. The measurements and indices assigned to each diffraction line are recorded in table I. Certain lines are quite diffuse; this feature has previously been noted by Byström and Westgren (1943) on synthetic material, and is a property of the substance rather than a grain-size effect, since most lines are sharp and clearly resolved.

Darbyshire (1932) reported on the differentiation of the different oxides of lead by X-ray powder diffraction. Unfortunately, he did not record measurements for Pb₃O₄, but as far as we can tell by comparison with his published photograph of the pattern for Pb₃O₄, it is identical with ours. Byström and Westgren (1943) published powder diffraction data for synthetic Pb₃O₄. Our measurements agree well with theirs, although

TABLE I. X-ray powder diffraction data for minium. Co- $K\alpha$ radiation, λ 1.7902 Å. Intensities visually estimated. Average of 3 films. 114.59 mm. diameter camera.

<i>hkl</i>	<i>d</i> , Å.	<i>I</i> .	<i>hkl</i>	<i>d</i> , Å.	<i>I</i> .
110	6.22	m	611	1.414	m
211	3.38	s	532	1.373	w
002	3.29	vw	621	1.365	vw
220	3.114	m	541	1.347	w
112	2.905	s	523	1.311	w(b)
310	2.787	s(b)	622	1.283	w(b)
202	2.633	m	424	1.262	w
320	2.446	w	710, 550	1.245	m
321	2.291	w	712, 552	1.166	m
222	2.258	w	325	1.157	w(b)
400	2.205	vwv	642	1.146	m
330	2.078	vw	444	1.130	m
411	2.033	w(b)	534	1.112	w
420	1.968	m(b)	006	1.094	w(b)
213	1.913	m	116	1.078	w
402	1.829	m(b)	206	1.061	vw(b)
332	1.755	s	742, 812	1.038	m
431, 501	1.702	vwv	525	1.025	w(b)
004	1.640	w	653	1.003	w
521	1.587	w(b)	554, 714	0.9921	w
440	1.558	m	752	0.9786	w(b)
413	1.531	w(b)	336	0.9683	m
530	1.512	w	761	0.9466	w(b)
600	1.470	w(b)	516	0.9252	w(b)
610	1.453	w	217	0.9123	w

they have recorded several weak lines that do not appear on our films, and similarly, we have recorded several that do not appear on theirs. This discrepancy is more probably due to the restrictions of the powder method than to any real difference in the substances, since in both cases all the diffraction lines can be indexed on the same unit cell.

All the diffraction lines can be satisfactorily indexed on a tetragonal cell with a 8.824 Å. and c 6.564 Å. These dimensions agree well with those of Byström and Westgren (1943), and Byström (1945), but are somewhat smaller than those of Straumanis (1942) and Gross (1943); after conversion of kX units to Å. we have:

Straumanis (1942)	.	.	.	a 8.893 Å.	c 6.52 Å.	c/a 0.733
Byström and Westgren (1943)	.	.	.	8.82	6.57	0.745
Gross (1943)	.	.	.	8.88	6.67	0.751
Byström (1945)	.	.	.	8.806	6.564	0.745
Present work	.	.	.	8.824	6.564	0.741

Gross (1943) determined the space group of synthetic Pb_3O_4 as $P\bar{4}b2$, with a pseudosymmetry of $P4/mbc$. Byström (1945) obtained better crystals than Gross and established the true symmetry as $P4/mbc$.

Lacking adequate material we cannot confirm this, but there seems no reason to doubt that the Broken Hill minimum is in every way identical with the synthetic material described by previous workers.

References.

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